1.0

1.1

1.25

1.4

1.28

1.32

1.36

1.40

2.0

2.2

2.0

1.8

1.6

MICROCOPY RESOLUTION TEST CHART

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	Approved for public release; distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
	ARO 19750.7-PH

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
University of Pennsylvania		U. S. Army Research Office

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Suite 300 Mellon Bank Building 133 South 36 Street Philadelphia, PA 19104-6292	P. O. Box 12211 Research Triangle Park, NC 27709-2211

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
U. S. Army Research Office		DAAG29-83-K-0075

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
P. O. Box 12211 Research Triangle Park, NC 27709-2211				

11. TITLE (Include Security Classification)
Nonlinear Optical Processes in Molecular Systems

12. PERSONAL AUTHOR(S)
Robin M. Hochstrasser

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM 5/9/83 TO 10/30/87	1988: January 15	

16. SUPPLEMENTARY NOTATION
The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17.	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Nonlinear optics; picosecond lasers; femtosecond lasers; ultrafast processes second harmonics; resonant molecular optics; Raman effects.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This research was concerned with studies of ultrafast processes in condensed matter studied by the various nonlinear optical spectroscopic methods. Work was completed in areas involving: the theory of strong field effects; the separation of fluorescence and Raman scattering; the effects of condensed matter fluctuations on Raman; fully resonant second harmonic generation; Dice effects in $\chi^{(3)}$ analysis of third order responses for rotating dipoles; picosecond studies of molecular reorientation; subpicosecond responses of metal particles to light; and effects of ultrahigh intensity pulses on the Raman spectral shape. (Keywords: picosecond lasers; resonant molecular optics; gold particles; Raman scattering).

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR
83 APR edition may be used until exhausted.
All other editions are obsolete.

AD-A193 871

1. Molecular reorientation

We have studied a variety of picosecond nonlinear optical responses which give information about the reorientation. Both new theory and new experiments were developed.

The population of excited states generated by nonlinear optical interactions are usually anisotropic. This anisotropy is manifested as a dichroism. Nonlinear signals that depend on such dichroism have response functions that decay on the reduced timescale of T_1 relaxation and the orientational correlation time of the transition dipoles that generate the resonances. Motional properties of systems are usefully described using the conventional susceptibilities in cases where the motion is slow compared with the electromagnetic field impulses and T_2 decay times. In that case the response function of the system is developed by iteration in the usual way except that the transition dipole factor is taken to be time dependent but slowly varying.

For a system of four levels, a and b coupled by the excitation fields 1 and 2 at time 0, c and d coupled by the probing field, 3, at time τ, the usual density matrix expansion yields a slowly varying portion of the response to linear polarized fields having the form:

$$\langle \mu_{ab}(0) \cdot \hat{e}_1 \mu_{ba}(0) \cdot \hat{e}_2 \mu_{cd}(\tau) \cdot \hat{e}_3 \mu_{dc}(\tau) \cdot \hat{e}_4 \rangle = |\mu_{ab}\mu_{cd}|^2 (A + Be^{-\tau/\tau_R}) \qquad (1)$$

where $\hat{e}_4$ is the polarization of the generated wave. This response refers to all experiments involving a field product $\mathcal{E}_1 \ \mathcal{E}_1{}^* \mathcal{E}_2$, including polarization spectroscopy, transient gratings and crossed gratings. Conventional Bragg diffraction in which a transient grating formed by excitation pulses of the same polarization ($\hat{e}_1 \cdot \hat{e}_2 = 1$) is probed with parallel ($\hat{e}_3 \cdot \hat{e}_2 = 1$) and perpendicular ($\hat{e}_3 \cdot \hat{e}_2 = 0$) polarizations has the advantage of yielding both the time dependence and the magnitude of the induced anisotropy. However the accompanying acoustic grating interferes with the polarization sensitive excited state grating. In the crossed grating configuration, the acoustic signal is eliminated by the use of perpendicularly polarized excitation pulses $\hat{e}_1 \cdot \hat{e}_2 = 0$. Polarization spectroscopy ($\hat{e}_1 \cdot \hat{e}_2 = 1$; $\hat{e}_4 \cdot \hat{e}_3 = 0$) gives the same susceptibility and anisotropy dynamics as the crossed grating but is more sensitive to interference from background birefringence because $k_4 = k_3$.

The orientation average of Eq. (1) is readily evaluated for the case of isotropic diffusion having relaxation time τ , to yield the following values for the constants A and B:

A = 1/3 ; B = $2r_0/3$ for conventional grating probed parallel
A = 1/3 ; B = $-r_0/3$ for crossed grating probed perpendicular
A = 0 ; B = $r_0/2$ for crossed grating and polarization spectroscopy

where $r_0 = (2/5) \langle P_2 [\mu_{ab}(0) \cdot \mu_{cd}(\tau)] \rangle$ and P_2 is the second Legendre polynomial. It is easy to deduce the relative signal intensities (at time zero) for each of these techniques. These techniques are each useful in determining rotational relaxation dynamics in molecular condensed phases. Furthermore when the four waves all have the same frequency, the methods provide a way of measuring T_2 for the pumped transition through studies of the "coherent spike" seen at zero delay time. The experiments of Myers and

Hochstrasser verified quantitatively each of the foregoing theoretical predictions.

2. Fully resonant $\chi^{(2)}$

In the presence of a dc electric field, $\chi^{(2)}$ phenomena such as sum- and difference-frequency generation will occur in all media. Although the observed effects are strictly third order in the applied fields, two optical and one dc, the coherent light generation pathways and the dynamical parts of the susceptibility determining the spectral shapes are characteristic of $\chi^{(2)}$ processes. Using this approach, spectroscopic applications of both sum- and difference-frequency generation under fully resonant conditions have been explored by us under the aegis of this Grant. The system used to demonstrate these effects was a mixed crystal of a polar guest (azulene) doped substitutionally into a centrosymmetric host (naphthalene). The average dipole moment of the mixed crystal is zero but in the presence of a dc electric field the random translational lattice of guest molecules is transformed into two interpenetrating but distinguishable sublattices consisting of polar molecules whose dipoles project parallel and antiparallel to the applied field. The optical transitions of the guest molecules in these two sublattices can then be separately observed. If this system is now subject to an intense electro-magnetic field having an arbitrary frequency it will respond as if it were non-centrosymmetric. Conventional electric-field-induced second-harmonic generation will occur, for example, with the SHG radiation intensity depending on the square of the dc-field strength. However, a qualitatively different effect is observed when the oscillating field is nearly resonant with one of the guest transitions corresponding to just one of the polar sublattices. In this case the field senses a material which is polar, and at sufficiently high dc fields the $\chi^{(2)}$ process, occuring as a result of the response of one sublattice, becomes nearly independent of the dc-field strength. The experiments were carried out with the optical field chosen to be resonant with spectrally sharp transitions of the S_1-S_0 and S_2-S_0 transitions of azulene. The permanent dipole moment of S_0, S_1 and S_2 are known to be sufficiently different that relatively small dc fields cause readily observable pseudo-Stark splittings of the spectral lines and separate effectively the two sublattices. The resonant contributions to $\chi^{(2)}$ of each sublattice separately are given by:

$$\chi^{(2)}_{SUM} = \frac{\mu^{(1)}_{01}\mu^{(2)}_{12}\mu^{(3)}_{20}}{(\omega_{10}-\omega_1+i\Gamma_{01})[\omega_{20}-(\omega_1+\omega_2)+i\Gamma_{02}]} \tag{2}$$

$$\chi^{(2)}_{DIF} = \frac{\mu^{(2)}_{20}\mu^{(1)}_{01}\mu^{(3)}_{12}}{(\omega_{10}-\omega_1+i\Gamma_{01})(\omega_{20}-\omega_2-i\Gamma_{02})}\left\{1+\frac{i(\Gamma_{12}-\Gamma_{01}-\Gamma_{02})}{[\omega_{21}-(\omega_2-\omega_1)-i\Gamma_{12}]}\right\} \tag{3}$$

Resonances should therefore occur at ω_{10} and ω_{20} in both sum and difference frequency generation and in addition a resonance at ω_{12} is predicted in the presence of pure dephasing (DICE resonance). In zero field, the contributions of the two sublattices have equal absolute values but are of opposite sign and cancel. In a dc field the shift of the transition frequencies ω_{ij} is opposite for the two sublattices resulting in a net non-zero value of $\chi^{(2)}$, which can be obtained from Eqs. (2) and (3) as:

$$\chi = \chi(\omega_{ij}-\Delta\mu_{ij}\cdot F) - \chi(\omega_{ij}+\Delta\mu_{ij}\cdot F) \tag{4}$$

where $\Delta\mu_{ij}$ is the difference of permanent dipole moment of azulene in states i and j, and F the electric field strength along $\Delta\mu$. Since the naphthalene host crystal is centrosymmetric the nonresonant field induced value of $\chi^{(2)}$ is very small and can be neglected. This predicted behaviour of $\chi^{(2)}$ is manifested in the experiment. All predicted resonances except the DICE resonance were observed in these experiments and the change of shape as a fuction of field strength can be fitted by formulas for $\chi^{(2)}$ as obtained from Eqs. (2)-(4) above. The absence of the DICE resonance was rationalized by numerical calculations of the spectra using paramaters derived from linear spectroscopic data, which predict it to be more than three orders of magnitude weaker than the main resonance and to be thus unobservable under the experimental conditions. The ω_{20} and ω_{10} resonances appear very similar in the sum and difference-frequency spectra, although complementarary line-narrowing properties are predicted for both spectra. This is because the purely homogeneous contribution to the non-linear linewidth dominates and any correlations within the inhomogeneous contributions have only a slight effect in this case. In systems where the inhomogeneous width dominates these experiments can be used for line-narrowing and to study inhomogeneous correlations.

3. Picosecond studies of gold particles

It was demonstrated that information about the coherence and energy relaxation of the surface plasmon of the aqueous colloidal gold system can be obtained from both frequency and time domain measurements. The $\chi^{(3)}$ dispersion, in conjunction with theory, has shown that the T_2 relaxation time is extremely rapid and less than 5×10^{-14} s. The comparable T_1 energy relaxation time most likely arises from the plasmon transferring its energy into the translational motions of the individual conduction electrons. These energetic electrons subsequently collide with the gold particle lattice to create lattice phonons. The eventual release of heat into the aqueous environment is suggested to be much slower and provides a bottleneck in the formation of thermal gratings.

Transient grating experiments performed on the dye solutions have helped confirm the behavior predicted by the theory. In these systems the assumed instantaneous formation of a uniform thermal grating is fulfilled because of the close proximity of the dye molecules and their rapid release of S_1 vibrational energy. Only for solutes which liberate heat more slowly (such as metal sols) can a nonradiative rate be determined. Using picosecond pulses, we have been able to temporally separate contributions arising from electronically resonant four-wave mixing and thermal/acoustic grating effects. More precise measurements and extensions of the theory to include noninstantaneous formations of thermal and acoustic transient gratings should help improve our knowledge of solvent constants and the dynamics associated with molecular nonradiative relaxation mechanisms.

The phase conjugate configuration with low repetition rate, high power picosecond lasers was used for performing the grating studies. Other grating configurations have larger grating spacings and in particular, the experiment with nearly colinear beams exhibits acoustic oscillations and thermal decays on the nanosecond or microsecond time scale. This implies that more rapid events go undetected. The eventual application of this approach to the study of UV absorbing molecular systems will also improve the time resolution needed to

measure even faster nonradiative processes in solution. This results from the creation of yet smaller grating spacings and higher frequency acoustic oscillations.

Lastly, the application of the transient grating method to the study of chemical reactions is proposed. The ability to detect relatively small amounts of liberated energy (only ~200 cm^{-1} per molecule or 0.6 kcal/mol for R6G) and to time resolve exothermic processes (exhibited by the gold sol experiment) makes this method potentially useful for studying a variety of picosecond photoinduced chemical isomerizations and reactions. The ability to monitor nonradiative exothermic photoinduced reactions between solute species may eventually be realized by applying variations of the present method.

4.   Dynamical aspects of Raman scattering

Our current activity in resonance Raman scattering spectroscopy includes studies that employ short laser pulses which means that samples are subject to intense laser fields and unusually fast events are seen directly. However a number of processes not necessarily important in conventional experiments require consideration when such excitation sources are employed. One possible effect arises because strong fields shift the molecular energy levels. Another possibility is that the Raman scattering will be influenced by the fact that incident photons have heated the sample. In addition, when the resonant spontaneous emission is gated on a time scale comparable with that of the free rotation of the molecule the dynamical evolution of the Raman process and its relation to fluorescence must be considered. There are also new effects to include when non-linear Raman methods are used with intense short pulses. In our work the physical basis for a number of these potentially important aspects of the Raman effect were evaluated.

As molecular spectroscopy moves into the femtosecond regime, it becomes important to consider the effects of nonlinear interactions between the molecules and the incident field which arise because of the large peak power of the laser pulses. In order to avoid such effects it is necessary to work at high repetition rates with pulses having extremely low energy. On the other hand there are things to be learned about the molecular dynamics from studies of the highly nonlinear response. In this section we will give a brief description of multiphoton processes and the effects of high fields on emission spectra.

It is likely that one of the most important influences of intense short laser pulses on molecules is photoionization. This is because it is very difficult to avoid multiphoton absorption with such pulses. For example, for a pulse carrying 50 μJ focused to 0.3 mm and having a temporal width comparable with the dephasing time of optical transitions, the population created by direct three photon absorption is 10% of that for one photon absorption assuming absorption cross sections of ca. 10^{-16} cm^2.

In some recent experiments with Cytochrome-c we have observed the power induced line broadening of resonant Raman lines[13]. By using 530 nm pulses of 30 ps duration at a variety of power densities to excite the sample the Raman scattering onto the 750 cm^{-1} mode was found to broaden noticeably for power densities in excess of 7×10^9 W cm^{-2}. This onset of broadening

corresponds to an inverse Rabi frequency of 125 fs which gauges the magnitude of the excited state dephasing time.

Raman spectroscopy and the related fluorescence carried out using intense short light pulses can yield interesting dynamical information not generally available from quasi-CW low power experiments. The spectra at sufficiently high fields begin to provide knowledge of the dynamics in the electronically excited states while the usual distinctions between fluorescence and Raman are lost. Resonance Raman and fluorescence spectra with short light pulses should manifest the free rotation of molecules even in condensed phases where the collision frequencies are not much larger than the free rotation frequencies. These effects of free rotation are predicted to influence CW Raman polarization measurements where the gating time for Raman is determined by the dephasing of the resonant transition.

Conclusions

This was intended to provide an overview of our studies, nonlinear optical studies of molecular systems with particular emphasis on condensed matter spectroscopic applications. We have shown that a wide range of material parameters can be determined by means of either time or frequency domain experiments which employ tunable lasers. The use of multiple laser fields allows the study of double or triple resonance effects and of dynamical processes involving molecular and excitonic excited states. The nonlinear optical theory provides the framework on which to understand all such multiresonant phenomena whether the radiation originate from the coherent polarization of the medium or by spontaneous decay.

For the future, there are a number of obvious directions that resonant molecular optics is likely to take. First, there is the study of extremely rapid responses using femtosecond light pulses. In addition it seems very interesting to proceed with the study of systems not close to equilibrium. This situation might involve materials that are heavily ionized or highly concentrated in excited states or excitons, and systems in which a large fraction of certain atoms, for example protons, are displaced from their equilibrium configurations. Another area of great interest barely touched on in this article is surface molecular optics. It is apparent that the principles presented here can be used to make detailed studies of surface states and of dynamical processes involving adsorbed molecules. Finally, an important area is the development and characterization of new molecular materials having the required resonances and dynamics to permit qualitative improvements in, as well as the generation of, new types of optical materials.

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